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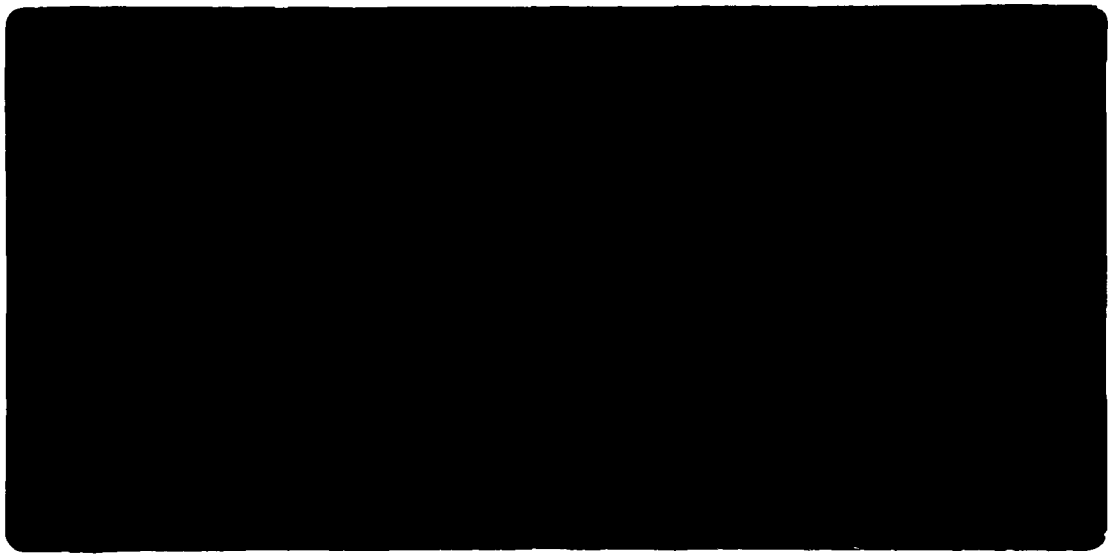

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MECHANISMS AND RATES OF RECOVERY BOILER FUME DEPOSITION

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by

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Abstract

A laboratory study of deposition rates was performed for the same types of fumes that occur in recovery furnaces. The experimental results indicate thermophoresis is the rate-controlling mechanism for deposition. Quantitative rate equations were developed and fit limited data on deposition rates in recovery boilers. The important variables controlling fume deposition rates are particle size and concentration, ΔT, tube wall temperature, and gas velocity (through the heat transfer coefficient).

Introduction

Fume is one of the products of kraft black liquor combustion. Fume consists of very small particles (generally in the size range of 0.1 μm to 1 μm diameter) and is composed mainly of sodium sulfate, sodium carbonate, and potassium salts. Chemical fume formation is of interest because fume is partly responsible for fireside deposits formed on the heat transfer surfaces in the recovery boiler. These deposits reduce the heat transfer coefficients, contribute to the plugging of gas passages, and require sootblowing for their removal.

Fume has a high specific surface area due to its submicron size, which makes it very reactive in the flue gas. Most of the alkali compounds are converted to sulfates by reaction with SO_x gases. The chemical composition of fume in the recovery boiler is influenced by sulfidity, the chemical composition of the black liquor, and the bed temperature.

In this paper, the results of a fundamental study of the deposition of Na_2CO_3, Na_2SO_4, and NaCl fume particles are presented. The objectives of this study were to determine the mechanisms responsible for fume deposition in the generating banks and economizers of recovery boilers and to determine the rate-controlling parameters. A fume deposition rate equation was also developed.

Previous Research

Reeve, et al., [1,2], Tran, et al., [3,4,5,6], and Isaak [7] have obtained data from deposits in a recovery boiler. They have determined two different types of deposits which can form:

1. "Carryover"—smelt and/or partially burned black liquor particles (in the mm size range) physically entrained in the flue gas.

2. "Condensation"—particles forming by condensation either directly on cooled surfaces, or indirectly in the flue gas stream. "Condensation" deposits therefore include both particles that were solid species in the gas stream and those that crystallized onto a cooled surface due to vapor species being present in the gas stream.

These authors inserted a probe into the furnace and found that in the lower superheater carryover is dominant. Deposits on the upstream side were black, hard, and thick and consisted mostly of black liquor particles that were entrained in the flue gas. Deposits on the downstream side were white and thinner, which the authors assumed to be condensation deposits.

Deposition at higher elevations in the superheaters was slightly different. A layer of white powder, which became thicker with time, was formed on both the upstream side and downstream side of the probe; the deposit thickness was greater on the upstream side than on the downstream side. The authors made no mention as to the processes by which these deposits were formed.

No deposition rate data were obtained in the generating bank, economizer region, or precipitator. However, the chemical composition of the deposits in these sections has been determined. Tran [8] found that the chemical composition of the deposits in the boiler bank, economizer, and precipitator were very similar to each other, but different from the composition of superheater deposits. Superheater deposits consisted of approximately 2% carbon, 45% Na_2SO_4, 47% Na_2CO_3, and 6% chloride and potassium salts, whereas deposits in the upper boiler sections consisted of 80% Na_2SO_4, 5% Na_2CO_3, and 15% chloride and potassium salts. This indicates either a different type of particle that is depositing or a chemical conversion of the already-deposited particles.

Although the composition of upper furnace deposits has been studied, the mechanisms of deposition taking place in a recovery boiler to create these deposits have never been defined or understood. Deposition mechanisms are not only dependent on particle size, but also on boiler temperatures and gas flow rates. Also, particles depositing by a given mechanism in a given flow regime may deposit by a different mechanism in a different flow regime. The effects of various recovery boiler process variables have never been related to the mechanism and rate of deposition, only to the chemical composition of the deposits.

Fundamental deposition studies indicate there are six principal mechanisms by which particles can be deposited from a high temperature gas stream to a cooler surface [9,10]. These mechanisms (the first four in order of increasing particle size) are as follows:

1. Molecular diffusion.
2. Brownian motion.
3. Turbulent diffusion—particles are propelled through a turbulent boundary layer and deposited on the surface.
4. Particle impaction—particles deposit due to their inertia.
5. Thermophoresis—particles move through a gas phase temperature gradient.
6. Vapor diffusion—vapor species, present in the gas phase, crystallize.

As mentioned earlier, the controlling mechanism in any given system is highly dependent on flow conditions. These conditions include both those found in the bulk of the moving gas and those near the deposition surface.

Objectives

The objective of this study was to determine the deposition mechanisms for particles similar to fume particles found in the kraft furnace and to relate the results to the recovery boiler. The experimental study was designed to determine the effect of flue gas temperature, deposition tube surface temperature, particle composition, particle size, particle concentration, and gas flow rate on the deposition rate.

Fumes of pure Na_2CO_3, Na_2SO_4, NaCl, and combinations thereof can all be generated on a laboratory scale. The fume composition in the laboratory can be controlled and varied; however, the fume particle size is, with current knowledge, impossible to vary. Fume particles previously generated in the laboratory [1,12] are between 0.25 μm and 1.0 μm in diameter, which are similar to the particle sizes that Bosch, et al., [13] measured in recovery boiler electrostatic precipitators. Particle sizes in the generating bank and economizer should be similar to those found in the precipitator; therefore, to the extent that deposition mechanisms are size dependent, the laboratory apparatus has the same controlling mechanisms as the boiler bank and economizer.

Experimental System

The experimental system used to generate fume particles and the applicable chemical reactions is described in previous articles by Cameron, et. al., [11,12]. Pure Na_2CO_3 fume was generated by using a Na_2CO_3/Na_2S melt and by purging N_2 and air through the melt. CO_2 was added to the gas phase. Pure Na_2SO_4 fume was also generated by using a Na_2CO_3/Na_2S melt and by purging N_2 and air through the melt. SO_2 was added to the gas phase, which converted Na_2CO_3 fume to Na_2SO_4 fume. NaCl fume was generated by using a Na_2CO_3/NaCl melt and by purging N_2 below the melt. NaCl vaporized into the N_2 stream and condensed as the flue gas cooled.

Figure 1 shows the system used for fume deposition. Molten smelt was contained inside a ceramic crucible and steel retort; the retort was inside an electric tubular furnace. Nitrogen and air were mixed in the line before being bubbled through the smelt, and the carbon dioxide or sulfur dioxide was added to the gas phase above the smelt. The upper half of this apparatus clamped onto the lower retort and included the deposition cylinder on which the fume was collected. The air flow rate through the tube could be varied to change the tube surface temperature, and heaters surrounded the upper half so the gas phase temperature could be varied.

Experimental Procedure

For these experiments, the following variables were studied: fume concentration, flue gas temperature, deposition tube surface temperature, gas flow rate, deposition time, and fume composition.

Electron micrographs of all fume deposits were taken. Image analysis was then used to determine particle size distribution. The amount of fume on the tube was determined gravimetrically by scraping the fume off the tube into a dish and weighing it to the nearest 0.0001 gram on an analytical balance.

Experimental Results

The rate of Na_2CO_3 deposition in the presence of a temperature gradient was found to be proportional to fume concentration (Figure 2) over the range tested and unaffected by gas flow rate (Figure 3) in the range tested.

Figure 4 shows the dependence of Na_2CO_3 fume deposition on tube temperature and bulk gas temperature. DEL T is the temperature difference between the bulk flue gas and the surface of the tube; TUBE T is the cooled tube surface temperature. These data were taken at three different flue gas temperatures: 253° C, 396° C, and 527° C.

The Na_2SO_4 deposition rate, like Na_2CO_3 fume deposition, was found to be independent of gas flow rate and proportional to fume concentration and $\Delta T/T_w$. This demonstrates that Na_2SO_4 deposits by the same mechanism as Na_2CO_3. The NaCl deposition rate was also found to be independent of gas flow rate and proportional to the fume concentration and $\Delta T/T_w$, showing that NaCl deposits in a manner similar to Na_2CO_3 and Na_2SO_4.

The results of simultaneous Na_2SO_4 fume and NaCl fume deposition are similar to Na_2SO_4 fume deposition and NaCl fume deposition. The deposition rate of Na_2SO_4/NaCl, like other fume species studied, was proportional to fume concentration and $\Delta T/T_w$ and independent of flue gas flow rate. All fume deposits consisted of spherical particles, implying that the particles were being formed in the gas phase and that vapor diffusion/crystallization was not occurring (which would have produced crystalline deposits).

Discussion

The following results were consistent for all of the species studied:

1. Total fume deposition is proportional to deposition time.
2. The fume deposition rate is unaffected by gas flow rate.
3. The fume deposition rate is proportional to $\Delta T/T_w$ (as would be the case for thermophoresis).
4. The fume deposition rate is the same on the upstream side and downstream side of the cooled cylinder, implying that impaction on the upstream side is a minor mechanism.
5. No fume deposition occurs when no temperature gradient is present; this strongly indicates that thermophoresis is the controlling mechanism.

The measured fume deposition rates can be fit to the following equations:

$$Na_2CO_3 \text{ dep. rate } (g/min/cm^2) = 0.00440\, C \left(\frac{\Delta T}{T_w}\right) \quad (1)$$

$$Na_2SO_4 \text{ dep. rate } (g/min/cm^2) = 0.00419\, C \left(\frac{\Delta T}{T_w}\right) \quad (2)$$

$$NaCl \text{ dep. rate } (g/min/cm^2) = 0.0146\, C \left(\frac{\Delta T}{T_w}\right) \quad (3)$$

$$Na_2SO_4/NaCl \text{ dep. rate } (g/min/cm^2) = 0.00279\, C \left(\frac{\Delta T}{T_w}\right) \quad (4)$$

The average deposited particle sizes of the four fume species and their variances are listed in Table I.

Gokoglu and Rosner [14] have derived an expression for particle flux due to a temperature gradient (thermophoresis) across laminar boundary layers ($0 < Re < 10{,}000$):

$$\text{Dep. rate} = \rho_m V \left(\alpha_T \frac{Pr}{Sc}\right) St_h \left(\frac{\Delta T}{T_w}\right) \omega_m \qquad (5)$$

A simplified form of this equation shows that, for particle sizes between 0.1 μm and 1 μm, the deposition rate is proportional to particle diameter, particle thermal diffusion coefficient, and gas phase heat transfer coefficient.

If the thermal coefficient (α_T, dimensionless) and fume particle size (d_p, microns) are separated from the constants in Equations 1-4, measured fume deposition rates for all of the species studied can be written as:

$$\text{Dep. rate } (g/min/cm^2) = 0.036\, \alpha_T\, d_p\, C \left(\frac{\Delta T}{T_w}\right) \qquad (6)$$

For the experimental apparatus, the heat transfer coefficient is calculated to be $7.9*10^{-5}$ cal/cm^2 min ° K, leading to the following equation derived from Eq. 6:

$$\text{Dep. rate } (g/min/cm^2) = 452h\, \alpha_T\, d_p\, C \left(\frac{\Delta T}{T_w}\right) \qquad (7)$$

Therefore, fume deposition in the experimental apparatus can be modeled by a thermophoretic equation; the main factors affecting the fume deposition rate are h, α_T, d_p, C, and $\Delta T/T_W$.

Extrapolation to a Recovery Boiler

Suppose fume deposited equally on the entire surface of recovery boiler bank tubes with the following conditions [15]:

1. Na_2SO_4 fume.
2. $\alpha_T = 0.41$.
3. $D_p = 0.42\ \mu m$.
4. $C = 0.05\ g/L$.
5. $T_\infty = 700°\ C$.
6. $T_w = 180°\ C$.
7. $h = 1.1*10^{-3}\ cal/cm^2\ min\ °K$.

The amount of fume that should be deposited, calculated by Eq. 7, is:

$$\text{Dep. rate} = 1.0 \times 10^{-3}\ g/min/cm^2 \qquad (8)$$

The actual temperature gradient pattern on the downstream side of the tube, however, is unknown because of boundary layer separation. Therefore, suppose fume only deposits on the upstream side of the tube ahead of the separation point of 110°F; fume will then deposit on 220° of the tube or 61% of the tube surface. The fume deposition rate would be 61% of Eq. 8, or:

$$\text{Dep. rate} = 6.1 \times 10^{-4}\ g/min/cm^2$$

These two numbers bound the fume deposition rate by thermophoresis.

An actual fume deposition rate at the boiler bank inlet [15] under similar conditions is:

$$\text{Dep. rate} = 6.7 \times 10^{-4}\ g/min/cm^2$$

which is within the calculated bounds for fume deposition by thermophoresis. This suggests that thermophoresis is the main mechanism for fume deposition in a recovery boiler.

Conclusions

Thermophoresis is the main mechanism for fume deposition in recovery boilers; the rate-controlling parameters are flue gas temperature, tube surface temperature, particle composition and size, particle concentration, and gas phase heat transfer coefficient. The experimental results are directly applicable to fume deposition in the generating bank and economizer section in recovery boilers, where flue gas temperatures range from 200° C to 700° C. However, if some fume particles in a recovery boiler agglomerate to sizes greater than 10 μm, deposition by particle impaction is possible.

The results indicate that the rate of fume deposition in the recovery boiler is proportional to $h^*(\Delta T/Tw)$. The tube wall temperature is determined by the boiler pressure (saturation temperature); therefore, at constant particle size and concentration the deposition rate is governed by the heat flux and boiler pressure. These results imply that deposition rates would tend to be lower in higher pressure boilers.

Acknowledgments

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List of Symbols

C = concentration of fume in flue gas (g/L)
d_p = particle diameter (μm)
h = heat transfer coefficient (cal/cm^2 min °K)
Pr = Prandtl number
Sc = Schmidt number
St_h = Stanton number for heat transfer
ΔT = difference between flue gas temperature and deposition tube surface temperature
T_w = cooled tube surface temperature (°K)
T_∞ = mainstream gas temperature (°K)
V = velocity parallel to wall
α_T = thermal diffusion factor
ρ_m = density at the outer edge of the Brownian diffusion boundary layer
ω_m = mass fraction of particles in mixture, at the outer edge of the Brownian diffusion boundary layer

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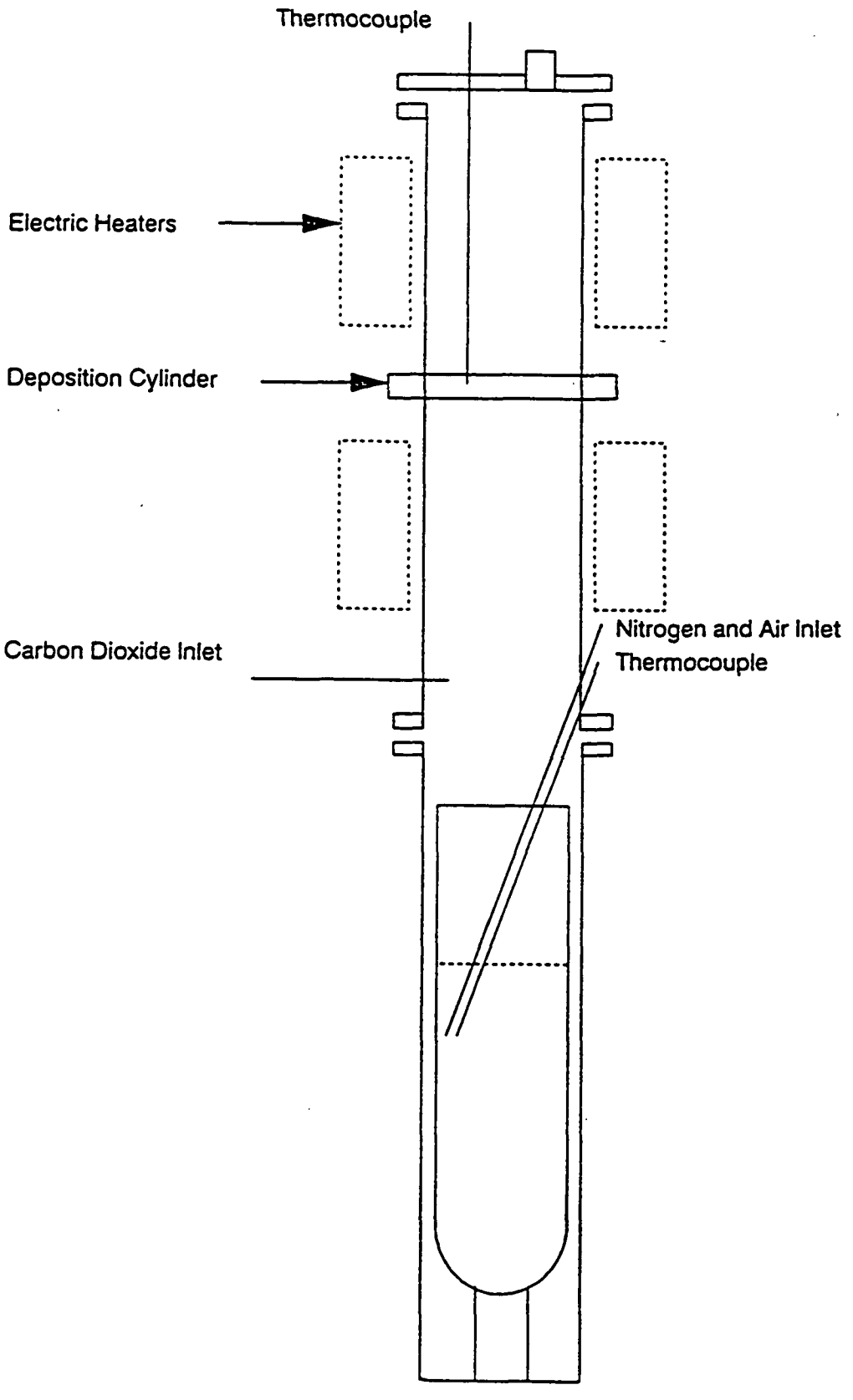
Figure Captions

Figure 1. Schematic of fume deposition apparatus.
Figure 2. Effect of fume concentration on Na_2CO_3 deposition.
Figure 3. Effect of gas flow on Na_2CO_3 deposition.
Figure 4. Effect of temperature on Na_2CO_3 deposition.

Table I. Deposited fume particle sizes.

Species	Number avg. diam., μm	95% confidence	Mass avg. diam., μm
Na_2CO_3	0.32	± 0.18	0.40
Na_2SO_4	0.29	± 0.20	0.42
NaCl	0.21	± 0.13	0.27
Na_2SO_4/NaCl	0.24	± 0.15	0.36



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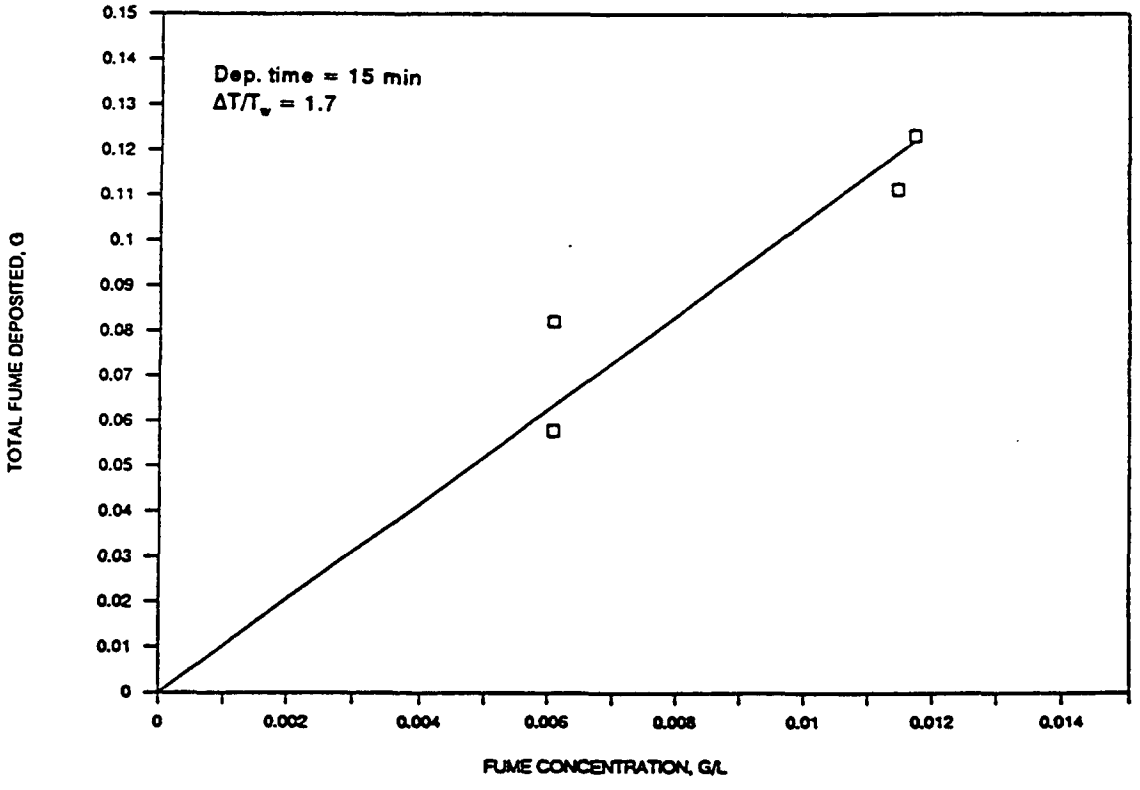

Figure 2. Effect of fume concentration on Na_2CO_3 deposition.

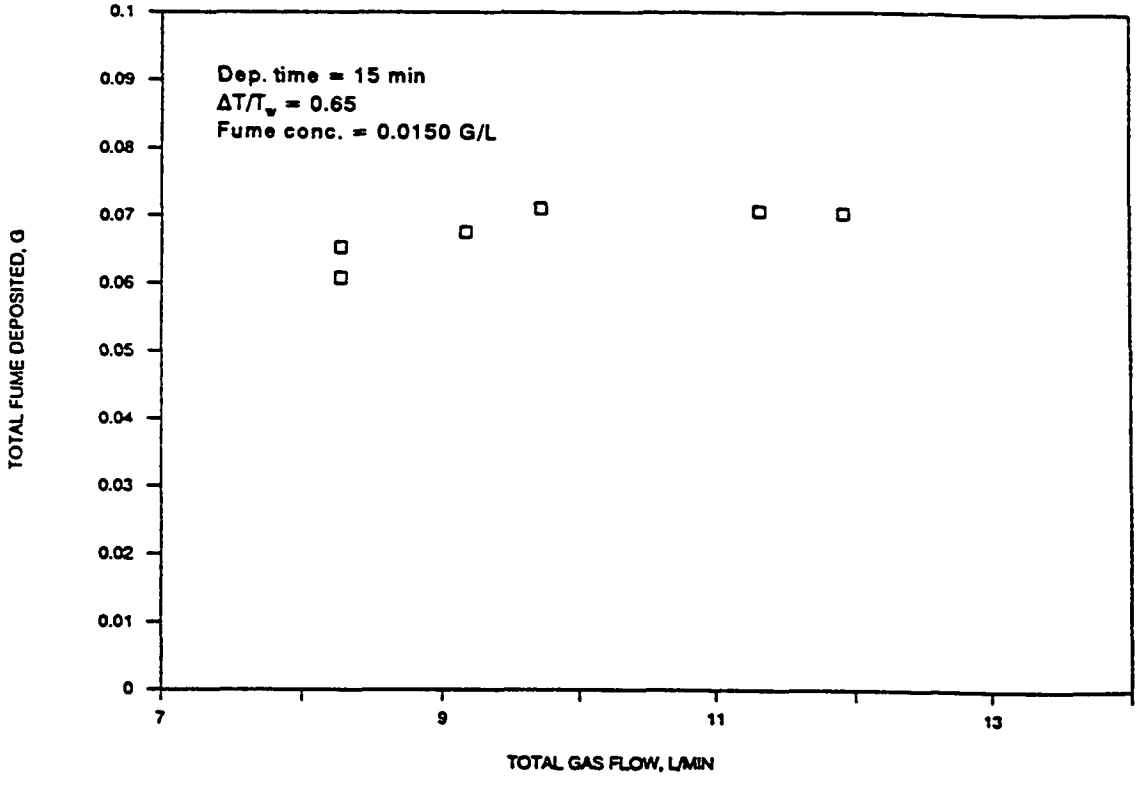

Figure 3. Effect of gas flow on Na_2CO_3 deposition.

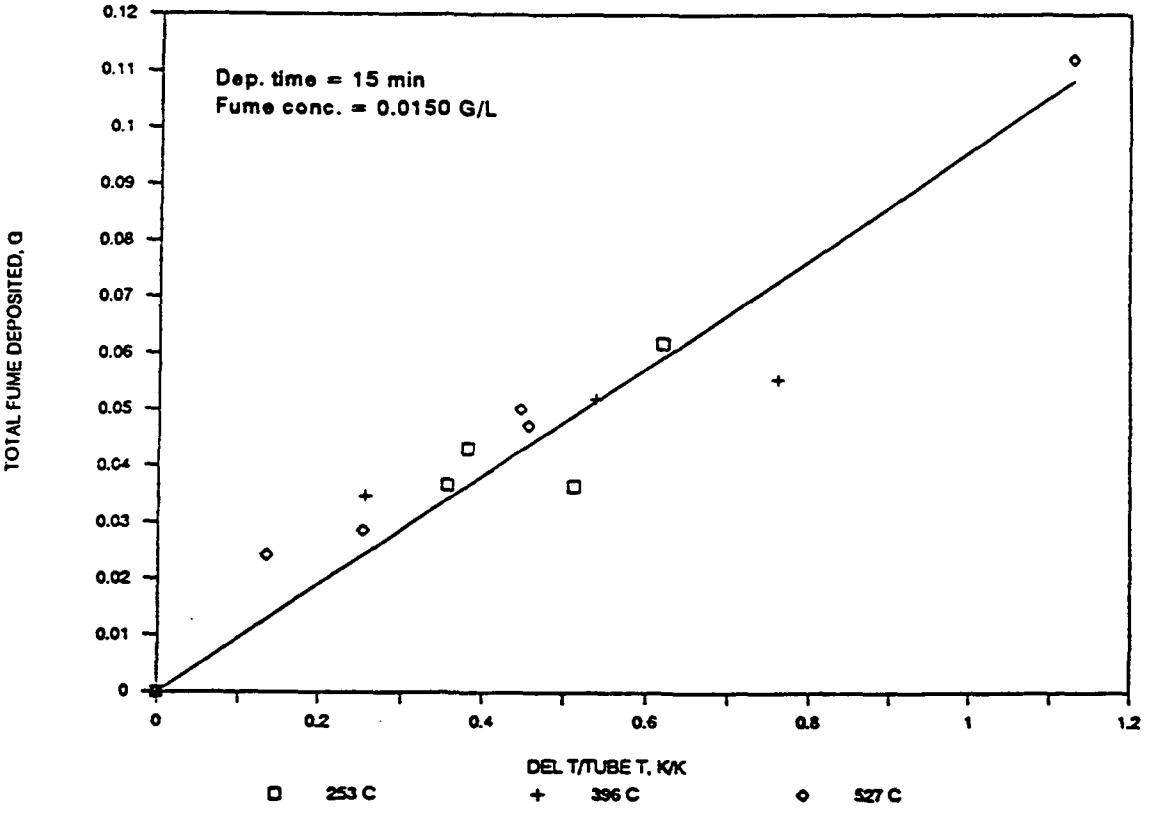

Figure 4. Effect of temperature on Na_2CO_3 deposition.